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Intrinsic Optical Absorption and the Radiative Recombination Lifetime in PbS

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The intrinsic optical absorption spectrum of PbS crystals has been measured. The absorption coefficients range from about 10 cm^{-1} to 10^5 cm^{-1} giving continuous data through the band edge. At 300°K the data indicate a direct transition energy of 0.41 ev and an indirect transition energy of 0.37 ev. The radiative recombination lifetime for PbS calculated from the absorption data is 63 microseconds at 300°K.

INTRODUCTION

THE optical absorption edge in a semiconductor is of interest since it provides information on direct and indirect electron transitions across the forbidden energy gap[1] and it can be used to calculate the radiative recombination lifetime of electrons and holes.[2]

While earlier investigations on the optical absorption edge in PbS represent notable advances in the subject,[3,4] these data are inadequate for analysis of the above quantities by current theories of optical absorption in semiconductors. The principal deficiency in these earlier data is the lack of measurements in the important range of absorption coefficients from about 10^2 to 10^4 cm^{-1}. Experimental difficulties due to the low transmission of PbS crystals limited Gibson's transmission measurements to wavelengths greater than 3 microns where the absorption coefficients were less than about 100 cm^{-1}.[3] Furthermore, since wide slits on the spectrometer had to be used to transmit energy through the crystal, the resolution was poor, about 0.4 micron near the band edge. In PbS at these wavelengths the absorption coefficient changes by almost two orders of magnitude in 0.4 micron so that the published transmission data may be questionable.

In the region of high absorption, about 10^4 to 10^6 cm^{-1} at wavelengths from 0.4 to 3.1 microns, the published results by Avery are based upon reflection measurements on cleaved crystal surfaces.[4] While these absorption data are satisfactory at high values of the absorption coefficient, he states that they may be in error by as much as 100% at the lower absorption coefficients.

In the vicinity of the band edge the two sets of data on the absorption edge overlap. In this overlap region of wavelengths the absorption coefficients obtained by the two methods of measurement differ by about two orders of magnitude. It is difficult, therefore, to estimate the detailed structure of the absorption edge in PbS from these measurements. One consequence of this is an uncertainty in the calculated value of the radiative recombination lifetime (mean life) of electrons and holes. Mackintosh,[5] using these results, estimates this lifetime to be about 40 microseconds with a possible error of a factor of 5. Burstein,[6] using the same results, estimates it to be 9 microseconds.

The purpose of the present study is to obtain more precise values for the absorption coefficient throughout the region of intrinsic absorption in PbS. From these results, values for direct and indirect optical transitions across the gap as well as the radiative recombination lifetime for electrons and holes can be calculated.

EXPERIMENTAL

Unlike germanium and silicon crystals, lead sulfide crystals split readily along {100} planes in the course of grinding and polishing operations. It is very difficult therefore to prepare thin crystals of PbS having a large area for conventional optical transmission measurements as was done for Ge and Si.[7] In order to make transmission measurements on thin crystals 2 or 3 mm on edge, it was necessary to adopt a microscope technique which permitted optical transmission studies on crystal areas as small as about 600×50 microns. For this purpose a Perkin-Elmer Model 85 infrared microscope attachment[8] was used in conjunction with a Perkin-Elmer recording spectrometer Model 12A. The infrared source was a globar operated at about 1000°C. A lithium fluoride prism gave the best resolution in the PbS absorption edge. For the slit width used in these experiments, the resolution ranged from 0.04 μ at a wavelength of 4 μ to 0.06 μ at 2.5 μ.

The crystal was placed at a reduced image of the monochromator exit slit where radiation from the monochromator was concentrated on the sample. The image reduction was 8.4 times. Radiation transmitted by the sample was magnified and conveyed by an optical system of mirrors to a detector. A special small-target thermocouple detector was used in these experiments. Scattered radiation was negligible. A

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[1] Bardeen, Blatt, and Hall, in *Photoconductivity Conference, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 146; D. Dexter, *Photoconductivity Conference, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 155; Fan, Shepperd, and Spetzer, *Photoconductivity Conference, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 184; H. Y. Fan, Repts. Progr. Phys. **19**, 107 (1956).

[2] W. van Roosbroeck and W. Shockely, Phys. Rev. **94**, 1558 (1954).

[3] A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

[4] D. G. Avery, Proc. Phys. Soc. (London) **B67**, 2 (1954).

[5] I. M. Mackintosh, Proc. Phys. Soc. (London) **B69**, 115 (1956).

[6] E. Burstein and P. Egli, *Advances in Electronics* (Academic Press, Inc., New York, 1955), Vol. 7, p. 56.

[7] W. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

[8] Coates, Offner, and Siegler, J. Opt. Soc. Am. **43**, 984 (1953).

built-in 175-power microscope viewer and illuminator made it possible to observe the sample by transmitted or reflected visible light. Thus the crystal area being studied could be accurately positioned and examined for pinholes or cracks.

The effect of nonparallel incident radiation on the crystal absorption was checked experimentally by making measurements on the same crystal with the microscope technique and with the conventional technique of parallel radiation. In both cases the sample-in, sample-out procedure was used. The maximum deviation between these two measurements was about $\pm 3\%$ at any given wavelength.

The crystals used in these studies included examples of natural and synthetic PbS. Even though the carrier concentrations ranged from 10^{17} to $10^{19}/\text{cm}^3$, there appeared to be no significant relation to the absorption. This is in agreement with Avery's[4] observations. The thicker crystals were prepared by cleaving while the thinner ones were prepared by grinding and polishing. The thinnest crystals, of the order of a micron thick, could not support themselves and were measured while glued to a polished plate of periclase crystal with a thin layer of glycol phthalate, a thermoplastic resin.[9] This glue had no objectionable absorption in this region of the spectrum.

The crystals of PbS were mounted on the supporting plate with the resin and ground flat with 600-mesh carborundum. Polishing was done on a rotating plate covered with silk velvet. The polishing compound was 1552 AB Gamma alumina No. 3. When no scratch marks could be seen under a low-powered microscope, the sample was turned over and given a final polish to the desired thickness.

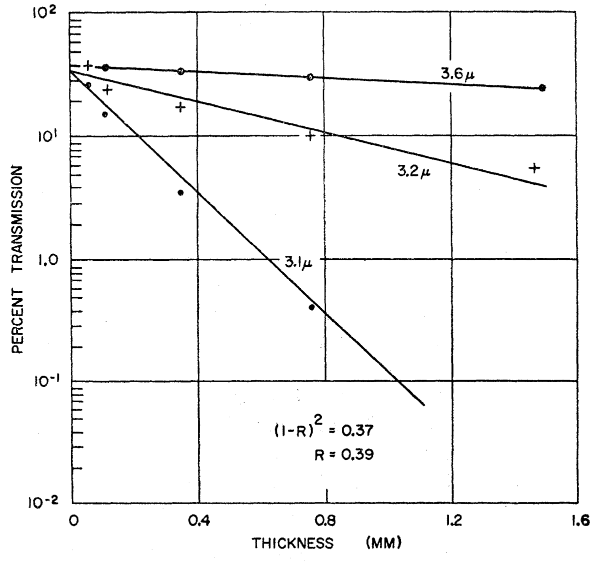

FIG. 1. Transmission through PbS as a function of thickness.

The cyrstal thickness was measured by various methods which did not require touching the crystal. Even slight pressure on these thin crystals produces prismatic punch indentations. The thicker crystals, of the order of a few hundred microns, were measured with a machinist microscope having a sensitivity of 0.1 mil/division. Crystals which were of the order of 10 microns thick gave interference fringe patterns and their thickness could be calculated with accuracy. Crystals which were a micron or less thick gave no interference pattern in the transparent region of wavelengths around 4 microns since the crystals were less than a $\frac{1}{4}\lambda$ thick. Their thickness was calculated from their absorption at wavelengths where data overlapped known absorption measurements on thicker crystals. In one instance a crystal was ground and polished so thin that it appeared deep red by transmitted light.

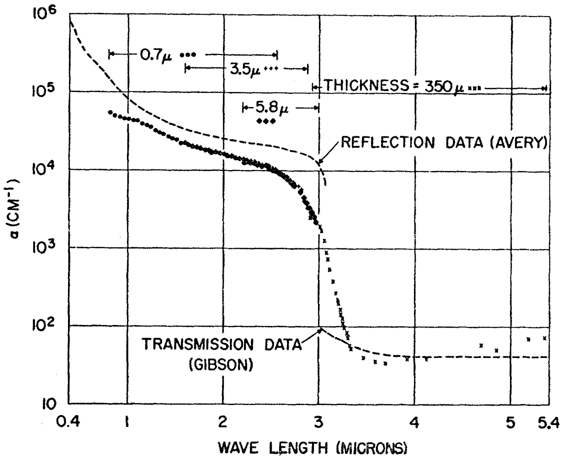

FIG. 2. Optical absorption coefficient for PbS as a function of wavelength.

RESULTS

In calculating the absorption coefficients, corrections were made for reflections. The reflectivity coefficient R, used in these calculations, was obtained by plotting transmission against thickness for various wavelengths and extrapolating to zero thickness. The data are shown in Fig. 1. The value of 0.39 for R calculated from these experiments agrees well with Avery's value of 0.39[10] and Paul, Jones, and Jones' value of 0.4 obtained by reflection measurements.[11]

The absorption coefficient as a function of wavelength is shown in Fig. 2. Here the data consist of contributions from several crystals of various thicknesses as indicated, with appreciable regions of overlap in the data.

For comparison, the transmission data of Gibson at low absorption values and Avery's reflection data at high absorption values are plotted on the same scale. We

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[9] The author wishes to thank Dr. Neuringer for generously supplying this resin.

[10] D. G. Avery, Proc. Phys. Soc. (London) **B66**, 138 (1953).

[11] Paul, Jones, and Jones, Proc. Phys. Soc. (London) **B64**, 528 (1951).

can see that the new data are in reasonable agreement with the previous measurements at high and low absorptions and in addition they give details on the shape of the absorption edge in PbS. The divergence of Gibson's data near the band edge is probably due to the low resolution in his measurements, 0.35 μ as compared to 0.04 μ in these measurements. The reflection data of Avery are reasonably accurate at high values of absorption but may be questionable at the lower values.

Direct and Indirect Transition Energies

From the shape of the absorption curve near the band edge it is possible to evaluate the energies for direct and possibly also indirect electron transitions. It has been shown theoretically by several authors[1] that in the case of direct transitions the absorption coefficients are generally large, of the order of 10^4, and the absorption coefficient is proportional to $E^{\frac{1}{2}}$ where E is the photon energy. The intercept on the energy axis gives the energy for the direct transitions. In Fig. 3 the data is presented as α^2 *vs* E for points including both high and low absorption. A straight-line relationship is observed for the high-absorption data. The zero intercept gives a value of 0.41 ev for the energy gap for direct transitions in PbS at 300°K.

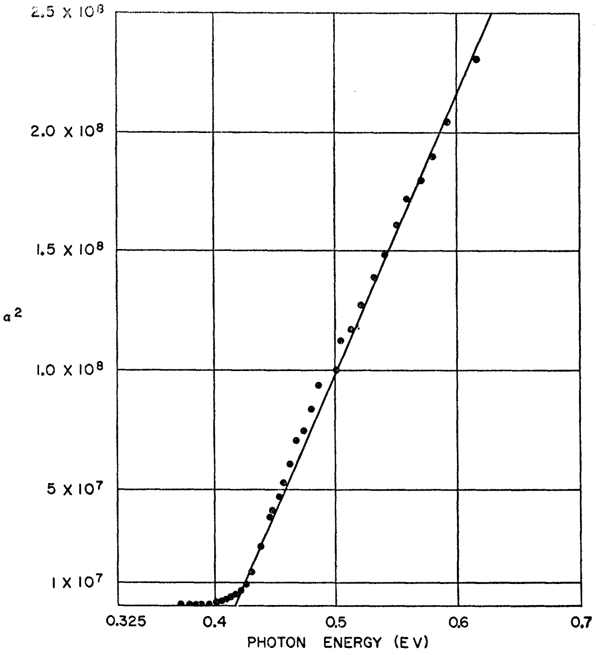

Fig. 3. The absorption coefficient squared as a function of photon energy for direct transition in PbS.

The theoretical interpretation of absorption through indirect transitions is not so clear. The absorption coefficients are low and the absorption equation may be a quadratic or cubic function of the photon energy. If we plot the absorption data for the lower end of the curve in Fig. 3 as $\alpha^{\frac{1}{2}}$ *vs* E, we have the curve of Fig. 4 which is approximately a straight line with a zero intercept, suggesting that the indirect-transition energy gap is 0.37 ev at 300°K.

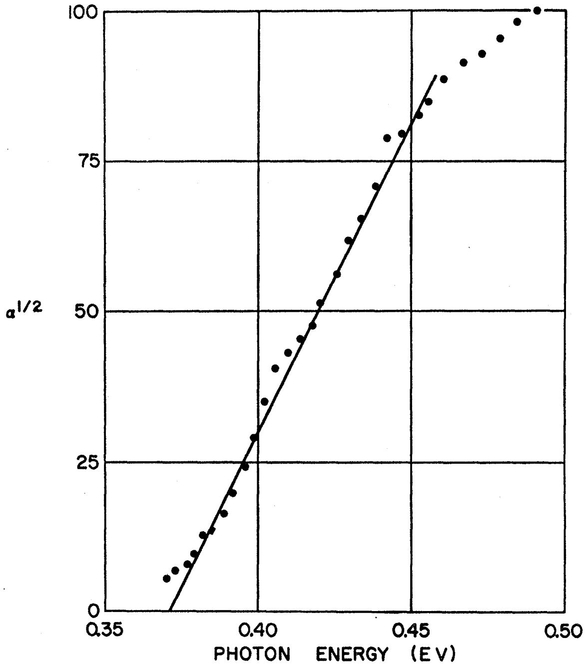

Fig. 4. The square root of the absorption coefficient as a function of energy for indirect transitions in PbS.

These results provide the first experimental values for energy gaps in PbS corresponding to direct and indirect transitions. An attempt was made by Bell and his co-workers[12] to calculate on a theoretical basis the energy-band structure in PbS. Their results suggested a direct transition energy of about 1.3 ev and an indirect transition energy of about 0.3 ev. Previous experimental studies of optical absorption, though incomplete, were interpreted by Avery[4] and Burstein[6] to verify Bell's theoretical calculations. When the absorption is plotted as a function of wavelength there is, in addition to the absorption edge at about 3 microns, an apparent second rapid rise in absorption at a wavelength of about 1 micron suggestive of an absorption edge of about 1 ev. However, if these same data are plotted in a more realistic way as a function of photon energy, there is no evidence of an absorption edge near 1 ev.

Radiative Recombination Lifetime

The van Roosbroeck-Shockley analysis of the optical absorption edge in terms of the radiative-recombination lifetime (τ_i) of electrons and holes[2] can be applied to these results for PbS. Their analysis gives for the lifetime

$$\tau_i = n_i / 2\mathcal{R}, \tag{1}$$

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[12] Bell, Hum, Pincherle, Sciama, and Woodward, Proc. Roy. Soc. (London) **A217**, 71 (1953).

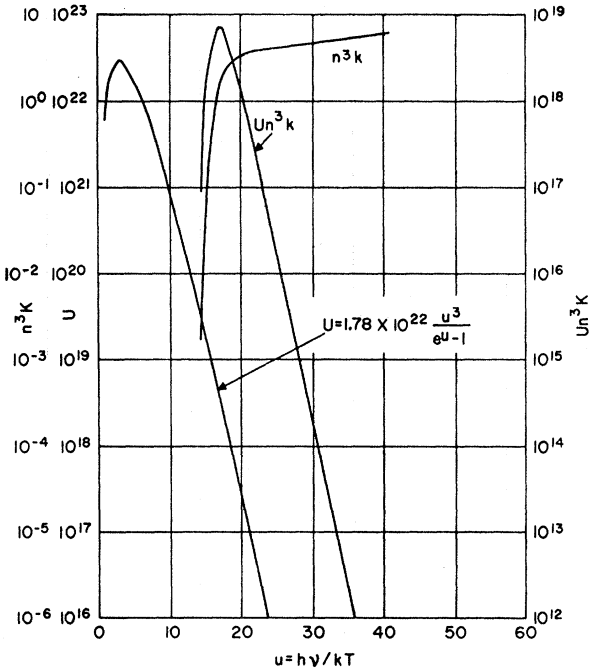

FIG. 5. The dependence for PbS of $n^3\kappa$ and the radiative recombination rate per unit frequency, $Un^3\kappa$, as a function of u.

where n_i is the concentration of electrons or holes in the intrinsic semiconductor. The value of n_i obtained from Hall effect studies[13] is $2.9\times10^{15}/\text{cm}^3$. $\mathcal{R}$ is the total rate of radiative recombination per unit volume at thermal equilibrium and is given by the integral

$$\mathcal{R}=32\pi^2c\left(\frac{kT}{ch}\right)^4\int_0^\infty\frac{n^3\kappa u^3du}{e^u-1}. \tag{2}$$

The refractive index n is 4.1 and according to Avery's studies is essentially constant for wavelengths from about 0.5 μ to 3.3 μ. The variable of integration is $u=h\nu/kT$. The absorption index κ is related to α by

$$\alpha=4\pi n\kappa\nu/c. \tag{3}$$

The integration of Eq. (2) can be performed numerically. For PbS the dependence of $n^3\kappa$ and the radiative recombination rate per unit frequency, $Un^3\kappa$, upon u are shown in Fig. 5. When one uses the absorption coefficient data obtained in these experiments, the numerical integration of (2) gives $\mathcal{R}=23\times10^{18}$ cm^{-3} sec^{-1} at 300°K.

From Eq. (1) the radiative recombination lifetime is $\tau_i=63$ microseconds at 300°K.

Measured carrier lifetimes in PbS crystals are less than this value, being limited by recombination at lattice dislocations by the Shockley-Read mechanism.[14] The maximum observed lifetime in a PbS crystal having a low density of dislocations is 20 microseconds.[15] Carrier lifetimes much larger than this are observed in evaporated or chemically deposited photoconductor films; however, they are now believed to be due to a trapping mechanism associated with deep-lying oxygen levels on the surface.[16]

CONCLUSIONS

The detailed shape of the intrinsic optical absorption edge in PbS has been determined experimentally from transmission measurements. The energy for direct transitions was found to be 0.41 ev at 300°K.

The theoretical basis for interpreting the low-absorption part of the absorption edge in terms of an indirect transition energy is not so clear and the value obtained, 0.37 ev at 300°K, may be modified when the analysis can be made more accurately.

Since the absorption edge is now known for PbS, the calculated value for the radiative recombination lifetime is believed to be well established. The value obtained is 63 microseconds. This value is greater than the largest experimentally observed value of 20 microseconds so that carrier lifetimes in present PbS crystals are limited by other recombination mechanisms.

ACKNOWLEDGMENTS

The author wishes to express appreciation for the many helpful discussions with Dr. F. Stern and Dr. R. L. Petritz of this laboratory.

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[13] Scanlon, Brebrick, and Petritz, *Photoconductivity Conference, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 619.

[14] W. Shockley and W. Read, Phys. Rev. **87**, 835 (1952).

[15] W. Scanlon, Phys. Rev. **106**, 718 (1957).

[16] J. N. Humphrey and R. L. Petritz, Phys. Rev. **105**, 1736 (1957).